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Percus–Yevick pair-distribution functions of a binary hard-sphere system covering the whole r-range

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Abstract. We present explicit formulae which allow an economical but very accurate evaluation of the pair-distribution functions $g_{ij}(r)$ for the whole range of distances of an additive binary hard-sphere system within the Percus–Yevick approximation. The method is based on the fact that for such a system the Laplace-transforms $\hat{g}_{ij}(t)$ of the $g_{ij}(r)$ are known analytically. The inversion of the Laplace-transform is performed in two different ways: the first one—preferably applied from the contact up to distances of a few diameters—calculates the inverse by means of an exact analytical procedure, whereas the other one—very useful for intermediate and large distances—uses an asymptotic method, truncating a rapidly converging series expansion. In the overlap region of the two methods we can obtain perfect agreement (i.e. up to machine precision), including the first few terms of this expansion. Both formulae are presented as general as possible to allow an easy extension to other binary hard-core systems.

1. Introduction

Ever since the first successes of liquid state theory at the end of the fifties, hard spheres (HS)—one- as well as two-component systems—have played a central role in this field: starting from the first simple models [1], followed by the first computer simulations (which were performed on hard-core systems [2]) they became in the following years a good, though simple model to describe the structure of liquid systems, in particular simple liquid metals [3]. Although liquid-state methods have by now become much more sophisticated and the description of liquid systems by simple pure HS models is by far bypassed, these systems still play an important role in present day liquid-state physics as is shown in the following examples:

(i) They are used as reference systems in one- and two-component variational [4] and perturbative methods [5].

(ii) HS bridge functions are used—due to the universality hypothesis of Rosenfeld and Ashcroft [6]—in thermodynamically self-consistent integral-equation approaches, such as the modified HNC [6, 7] and the reference HNC [8].

(iii) Recently, non-additive mixtures of hard spheres have been used to describe highly non-ideal liquid and amorphous mixtures [9, 10].

One of the main reasons why HS systems are so attractive in liquid-state physics is due to the fact that their direct correlation functions $c(r)$ (or $c_{ij}(r)$, for a mixture) may be calculated analytically within the Percus–Yevick (PY) approximation in the

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one-component case [11, 12] as well as in the *additive* binary [13] or even multi-component [14] case, where 'additive' means that the HS diameters R_{ij} ($R_{ii} = R_i$) have to fulfill the relation $R_{ij} = \frac{1}{2}(R_i + R_j)$. Such a solution for the $c_{ij}(r)$ may, by the way, also be obtained for the hard-sphere k-Yukawa-tail (HSYk) system in the mean spherical approximation [15, 16]. Yet, in the applications (variational or perturbative calculations) the main interest is rather focussed on the pair-distribution functions (PDF) $g(r)$ ($g_{ij}(r)$).

These functions may be obtained in different ways: the most direct one (and, at the same time, the most expensive one for what concerns the computing time) is to solve the PY integral equations numerically (e.g. by using Gillan's algorithm [17]). This procedure has the only advantage of being the most general one, i.e. it allows us to obtain structure functions for general (i.e. non-additive) binary HS systems [9, 10]. However, it is demanding from the point of view of the computational and programming effort and requires a continuous control of the numerical parameters to ensure accurate results.

A more economic procedure is to determine first the analytic Fourier-transforms of the $c_{ij}(r)$ and then perform the numerical transformation (using a Fast Fourier technique) to obtain the $g_{ij}(r)$ via the well known expressions (see e.g. [18] for an accurate implementation of this approach). This method is faster than the numerical solution of the PY equations but is not superior with respect to the numerical accuracy. Indeed, both these methods may be affected by a loss of numerical accuracy, in particular at large distances; that can be troublesome, for example, when high momenta of $[g_{ij}(r) - 1]$ are required.

For completeness sake we should mention the Perram method [19]: it is based on a recursive numerical integration of a one-dimensional linear integral equation for $g_{ij}(r)$. This equation is obtained within the Baxter factorization method [20] to solve the mean spherical approximation and the algorithm is not limited to pure HS systems. This method is very simple to program but it has two main drawbacks: the computational cost increases quadratically with the number of the grid points and the non-uniform accumulation of numerical errors makes it not suitable to obtain high accuracy at large distances. Only for pure HS a modified Perram method has been proposed by Glandt and Kofke [21] which reduces the problem of accumulation of errors and makes the computing time a linear function of the number of grid points. However, this optimized version cannot be easily extended to other interaction potentials.

Application of perturbative or variational methods requires yet a very fast and accurate evaluation of the pair distribution functions, since they might be demanded a hundred times or more in the determination of the reference system parameters.

The method which we shall present in this paper for the determination of the $g_{ij}(r)$ is a combination of two different representations of these functions obtained from the analytic solutions of the PY equations. These solutions provide us also with closed forms of the Laplace transforms $\hat{g}_{ij}(t)$ of the $g_{ij}(r)$ in terms of basic functions, i.e. of polynomials and exponentials. The *first* representation—which we shall call henceforward the shell-structure expression (SE)—was already worked out by Wertheim [11]: the inverse Laplace-transform is performed exactly by using the residue theorem. The special form of the integrand allows a shell-by-shell analytic integration, where the lower bound of a shell is marked by an integer-linear combination of the R_i. The application of this approach is limited to distances up to five or six times the core

radius by the rapidly increasing complexity of the expressions (especially in the binary case) and by numerical accuracy requirements. This method has already been applied successfully to the one-component case by Smith and Henderson [22] and extended to larger distances and to the HSY case by one of the authors [23]. Generalization to the binary HS case is straightforward (although the formalism is, of course, much more complicated) and has been presented for the first time by Throop and Bearman [24]; however, they did not give explicit expressions. The next contribution to tackle this problem has been made by Leonard *et al* [25]: their formulae are general and may be applied—at least in principle—up to any distance; yet we felt that it would be useful to re-examine their prescription to take care of many repeated expressions to get a substantial saving of computing time. Moreover, especially beyond a certain distance this method is no more economical. Finally, the cited authors do not discuss the numerical problems connected to this method (i.e. up to what distances their procedure may be applied without loss of numerical accuracy).

Here we present optimized and general expressions for the SE. We mean optimization and generality in the following sense: (i) optimization guarantees a fast numerical evaluation on a computer; (ii) generality makes possible an easy implementation of the relevant formulae for other hard-core systems (as HSY*k* or charged HS systems).

The first aim, optimization, is obtained by a close study of the structure of the expressions: we extract all the time-consuming calculations and manipulations which are common to the three different $g_{ij}(r)$ ((ij) = 1–1, 2–2 and 1–2); and even between those different cases symmetry relations may be detected, which help to avoid redundant calculations and to minimize the computing time. This should make applications for variational and perturbative calculations very economical and therefore attractive, even if the evaluation of the $g_{ij}(r)$ is requested very often. The second aim, generality, originates from the fact that the expressions for the $\hat{g}_{ij}(t)$ for a HSY1 system are formally identical to those of the simpler HS system: only the degree of the polynomials appearing in the expressions is of two degrees higher. The formulae presented here are enough general, so that the corresponding expressions for the HSY1 case can be easily evaluated following the same scheme.

The second method is based on the fact that the radial distribution functions may be represented as a series of oscillating exponentially damped functions. Such an expression is obtained by an elementary application of the residue theorem. Since the terms with the smallest damping are the leading terms for large distances, we refer to this formula as the asymptotic expression (AE). The advantage of this method is that the functional form for different terms is always the same and each additional term added to the above expansion requires a fixed amount of computational effort. The price we have to pay is that the coefficients and the parameters required for this expansion have to be obtained numerically from the roots of a non-algebraic equation; also this method is not new (it was discussed, for example by [26] in the case of a one-component system of HS). However, as far as the present authors know, it has not been applied yet to the case of a mixture and, more important, it was never combined to the SE method to derive a practical way of generating values of the PDF over the whole range of distances.

Indeed, these two algorithms are complementary. The SE may be used (with the expressions given here) for r-values less than $(\alpha_1 R_1 + \alpha_2 R_2)$, $\alpha_1 + \alpha_2 = 7$. Beyond this distance this method is not recommended: (i) the number of contributions to the sums and the complexity of the expressions has increases drastically and (ii) a loss in

numerical accuracy may be expected (depending on the number of significant digits of the computer used). On the contrary, in the AE we already obtain good convergence at large r with a rather small number of poles. With decreasing r the AE requires an increasing number of terms for a good convergency. In particular, due to a Gibb's phenomenon the AE is not suitable to represent the $g_{ij}(r)$ near and at the contact. However, we can show that there is an overlap region where both methods are about equally favourable concerning computing time and numerical accuracy and where it is possible to match the two expressions with arbitrary high accuracy. In this way we obtain an efficient and essentially exact representation of the PY radial distribution functions for all the distances.

The paper is organized as follows: in the next section 2 we review both methods for the determination of the $g_{ij}(r)$, the following section contains the discussion of the results: a comparison of the methods and investigations on the applicability of the respective approximations. The paper is closed by conclusions and by an appendix which contains the more complex expressions.

2. Methods

2.1. The shell-structure method

As already shown by Lebowitz [13], we may write the Laplace-transforms $\hat{g}_{ij}(t)$ of the pair-distribution functions $g_{ij}(r)$ in the following form

$$\hat{g}_{11}(t) = t[L_0(t) - L_2(t)\exp(tR_2)]/D(t) = N_{11}(t)/D(t) \tag{1}$$

$$\hat{g}_{12}(t) = 12\sqrt{\eta_1\eta_2}t^2L_3(t)\exp(tR_{12})/D(t) = N_{12}(t)/D(t) \tag{2}$$

$$\hat{g}_{22}(t) = t[L_0(t) - L_1(t)\exp(tR_1)]/D(t) = N_{22}(t)/D(t) \tag{3}$$

where we use the following notation

$$\eta_1 = \frac{\pi}{6}n_1 \tag{4}$$

$$\eta_2 = \frac{\pi}{6}n_2 \tag{5}$$

$$\eta = \eta_1R_1^3 + \eta_2R_2^3 \tag{6}$$

where the n_i are the number densities of species i, R_i is the hard-sphere radius of the corresponding particle type and $R_{12} = \frac{1}{2}(R_1 + R_2)$. The polynomials in (1)–(3) are given by

$$D(t) = L_0(t) - L_1(t)\exp(tR_1) - L_2(t)\exp(tR_2) + S(t)\exp[t(R_1 + R_2)] \tag{7}$$

$$L_0(t) = 36\eta_1\eta_2(R_2 - R_1)^2 \tag{8}$$

$$L_1(t) = 12\eta_2[(1 + \tfrac{1}{2}\eta) + \tfrac{3}{2}\eta_1R_1^2(R_2 - R_1)]R_2t^2 + [12\eta_2(1 + 2\eta) - L_0(t)R_1]t + L_0(t) \tag{9}$$

$$L_2(t) = 12\eta_1[(1 + \tfrac{1}{2}\eta) + \tfrac{3}{2}\eta_2R_2^2(R_1 - R_2)]R_1t^2 + [12\eta_1(1 + 2\eta) - L_0(t)R_2]t + L_0(t) \tag{10}$$

$$L_3(t) = [\tfrac{3}{4}(\eta_2R_2^3 - \eta_1R_1^3)(R_2 - R_1) - R_{12}(1 + \tfrac{1}{2}\eta)]t - (1 + 2\eta) \tag{11}$$

$$S(t) = L_0(t) + [12(\eta_1 + \eta_2)(1 + 2\eta) - L_0(t)(R_1 + R_2)]t - 18(\eta_1R_1^2 + \eta_2R_2^2)^2t^2 - 6(\eta_1R_1^2 + \eta_2R_2^2)(1 - \eta)t^3 - (1 - \eta)^2t^4. \tag{12}$$

According to Throop and Bearman [24] $1/D(t)$ may be expanded for sufficiently large $\Re(t)$ in the form

$$\frac{1}{D(t)} = \frac{\exp[-t(R_1+R_2)]}{S(t)} \sum_{n=0}^{\infty} \left[\frac{I(t)}{S(t)}\right]^n \tag{13}$$

with

$$I(t) = L_2(t)\exp(-tR_1) + L_1(t)\exp(-tR_2) - L_0(t)\exp[-t(R_1+R_2)] \tag{14}$$

so that we obtain for the pair-distribution functions in r-space

$$rg_{11}(r) = \frac{1}{12\eta_1} \sum_{n=0}^{\infty} \frac{1}{2\pi i} \int \frac{t[L_0(t) - L_2(t)\exp(tR_2)]I^n(t)\exp\{t(r-[R_1+R_2])\}}{[S(t)]^{n+1}}\,dt \tag{15}$$

$$rg_{12}(r) = \sum_{n=0}^{\infty} \frac{1}{2\pi i} \int L_3(t) \frac{I^n(t)t^2\exp[t(r-R_{12})]}{[S(t)]^{n+1}}\,dt \tag{16}$$

$$rg_{22}(r) = \frac{1}{12\eta_2} \sum_{n=0}^{\infty} \frac{1}{2\pi i} \int \frac{t[L_0(t) - L_1(t)\exp(tR_1)]I^n(t)\exp\{t(r-[R_1+R_2])\}}{[S(t)]^{n+1}}\,dt. \tag{17}$$

The integrations in (15)–(17) have to be taken along a line in the right half-plane (RHP) of the complex t-plane, parallel to the imaginary axis and to the right of all the poles of the integrand, i.e. the four zeros of $S(t)$, t_i [13].

We start treating expression (15) for $g_{11}(r)$ and obtain

$$rg_{11}(r) = \frac{1}{12\eta_1} \sum_{n=0}^{\infty} \frac{1}{2\pi i} \int \frac{1}{[S(t)]^{n+1}} \sum_{\alpha_1,\alpha_2} tQ_{n,\alpha_1\alpha_2}(t)\exp\{t[r-(\alpha_1R_1+\alpha_2R_2)]\}\,dt$$
$$\alpha_1 = 1,\ldots,n+1 \qquad \alpha_2 = n+1-\alpha_1,\ldots,n+1. \tag{18}$$

The $Q_{n,\alpha_1\alpha_2}(t)$, being products of $L_0(t), L_1(t)$ and $L_2(t)$, are polynomial of order $2[2n+2-(\alpha_1+\alpha_2)]$ in t.

We now make closer investigations on the integrals in (18), picking out one single summand:

(i) If $r < (\alpha_1R_1 + \alpha_2R_2)$ we have, keeping the integrand finite, to close the integration path over a semicircle in the RHP, thus forming a contour which contains no poles of the integrand. Therefore the summand will not contribute to $g_{11}(r)$.

(ii) However, if $r \geqslant (\alpha_1R_1 + \alpha_2R_2)$, we have to close the integration path with a semicircle on the left half-plane (LHP), a contour which contains all the four poles of $S(t)$. In this case we shall obtain contributions to $g_{11}(r)$, which can be evaluated by means of the the residue theorem. Therefore we are left to calculate the residues $R^i_{n,\alpha_1\alpha_2}$ of terms as $\{tQ_{n,\alpha_1\alpha_2}\exp[t(r-X)]/S^{(n+1)}(t)\}$ for $t = t_i$, where we use a short-hand notation X for $\alpha_1R_1 + \alpha_2R_2$:

$$R^i_{n,\alpha_1\alpha_2} = \frac{1}{n!}\lim_{t\to t_i}\left(\frac{d^n}{dt^n}\left\{(t-t_i)^{n+1}\frac{tQ_{n,\alpha_1\alpha_2}(t)\exp[t(r-X)]}{S^{n+1}(t)}\right\}\right). \tag{19}$$

We shall obtain expressions containing linear combinations of products of the $L_i(t)$, $i = 0, 1, 2$ and their respective derivatives, products and quotients of $S(t)$ and its derivatives (all of them taken for $t = t_i$) and powers of $[r-(\alpha_1 R_1+\alpha_2 R_2)]$; we shall express them as suitably chosen coefficients a_n^i and $b_{n,\alpha_1\alpha_2}^{j,i}$ so that we finally arrive at the following expression for $g_{11}(r)$

$$rg_{11}(r) = \frac{1}{12\eta_1}\frac{1}{n!}\sum_{n=0}^{\infty}\sum_{\alpha_1,\alpha_2}\sum_{i=1}^{4} a_n^i \exp\{t_i[r-(\alpha_1 R_1+\alpha_2 R_2)]\} \times \sum_{j=0}^{n} b_{n,\alpha_1\alpha_2}^{j,i}[r-(\alpha_1 R_1+\alpha_2 R_2)]^j \Theta[r-(\alpha_1 R_1+\alpha_2 R_2)]. \tag{20}$$

The coefficients a_n^i and $b_{n,\alpha_1\alpha_2}^{j,i}$ and the explicit form of the polynomials $Q_{n,\alpha_1\alpha_2}(t)$ are compiled in the appendix. In fact we have manipulated the expressions (15)–(17) in such a way that the a_n^i are the same in all three cases which helps us to save computing time. The range for α_1 and α_2 in the above sum is the same as in (18) and $\Theta(x)$ is the usual Heaviside step function, being 1 for positive argument and 0 for negative x. In analogy to the one-component case (cf [22, 23]) we rewrite (20) as

$$rg_{11}(r) = \sum_{n=0}^{\infty}\sum_{\alpha_1\alpha_2} rg_{n,\alpha_1\alpha_2}^{11}(r)\Theta[r-(\alpha_1 R_1+\alpha_2 R_2)] \tag{21}$$

where we have defined

$$g_{n,\alpha_1\alpha_2}^{11}(r) = \frac{1}{12\eta_1}\frac{1}{n!}\sum_{i=1}^{4} a_n^i \exp\{t_i[r-(\alpha_1 R_1+\alpha_2 R_2)]\}\sum_{j=0}^{n} b_{n,\alpha_1\alpha_2}^{j,i}[r-(\alpha_1 R_1+\alpha_2 R_2)]^j. \tag{22}$$

In contrast to the one-component case, where the shell structure was very simple (i.e. given by the multiples of the HS diameter) the situation is, except for the trivial case $R_1 = R_2$, in the binary case more complex: given R_1 and R_2 we have for every fixed n-value $[(n+1)(n+4)/2]$ n-subshells, characterized by α_1 and α_2

$$S_{n,\alpha_1\alpha_2} := \{r \mid r \geqslant (\alpha_1 R_1+\alpha_2 R_2)\} \qquad 1 \leqslant \alpha_1 \leqslant n+1 \quad n+1-\alpha_1 \leqslant \alpha_2 \leqslant n+1. \tag{23}$$

In the binary case n looses its importance of an ordering parameter of the shells.

(i) An n'-subshell may extend from smaller r-values than a n-shell even though $n' > n$.

(ii) Above all, two subshells $(S_{n,\alpha_1\alpha_2}, S'_{n',\alpha'_1\alpha'_2})$ $(n \neq n')$ may coincide, since for their identity it is sufficient that $\alpha_1 = \alpha'_1$ and $\alpha_2 = \alpha'_2$.

(ii) A considerable overlap of n- and n'-subshells $(n \neq n')$ may occur especially if the values of R_1 and R_2 are quite different.

The smallest left boundary of the n-subshells is given by

$$r_{0,n} = \min_{\alpha_1,\alpha_2}\{\alpha_1 R_1+\alpha_2 R_2\} \qquad 1 \leqslant \alpha_1 \leqslant n+1 \quad n+1-\alpha_1 \leqslant \alpha_2 \leqslant n+1. \tag{24}$$

The expressions presented have been evaluated up to $n = 6$; therefore, the use of these expressions is limited to r-values, satisfying

$$r < r_{0,6}. \tag{25}$$

If this is not respected, contributions of higher subshells would be neglected and would consequently yield false results.

For the determination of the corresponding equations for $g_{22}(r)$ we proceed in a similar manner. We obtain an equivalent expression to (22), namely

$$g^{22}_{n,\alpha_1\alpha_2}(r) = \frac{1}{12\eta_2}\frac{1}{n!}\sum_{i=1}^{4} a_n^i \exp\{t_i[r-(\alpha_1 R_1+\alpha_2 R_2)]\}\sum_{j=0}^{n}\tilde{b}^{j,i}_{n,\alpha_1\alpha_2}[r-(\alpha_1 R_1+\alpha_2 R_2)]^j$$
$$\alpha_2 = 1,\ldots,n+1 \qquad \alpha_1 = n+1-\alpha_2,\ldots,n+1. \tag{26}$$

Note the different range of the α_i-values compared to the 1–1 case. The coefficients a_n^i and $\tilde{b}^{j,i}_{n,\alpha_1\alpha_2}$ are obtained from residues similar to (19), where the $Q_{n,\alpha_1\alpha_2}(t)$ are replaced by $\tilde{Q}_{n,\alpha_1\alpha_2}(t)$ (for their explicit form see the appendix). The subshell structure is given similar to (23) by

$$\tilde{S}_{n,\alpha_1\alpha_2} := \{r \mid r \geqslant (\alpha_1 R_1+\alpha_2 R_2)\} \qquad 1 \leqslant \alpha_2 \leqslant n+1 \quad n+1-\alpha_2 \leqslant \alpha_1 \leqslant n+1. \tag{27}$$

Figure 1 displays as an example the PDFs $g_n^{22}(r) = \sum_{\alpha_1,\alpha_2} g^{22}_{n,\alpha_1\alpha_2}(r)$ for different n-values for one special system.

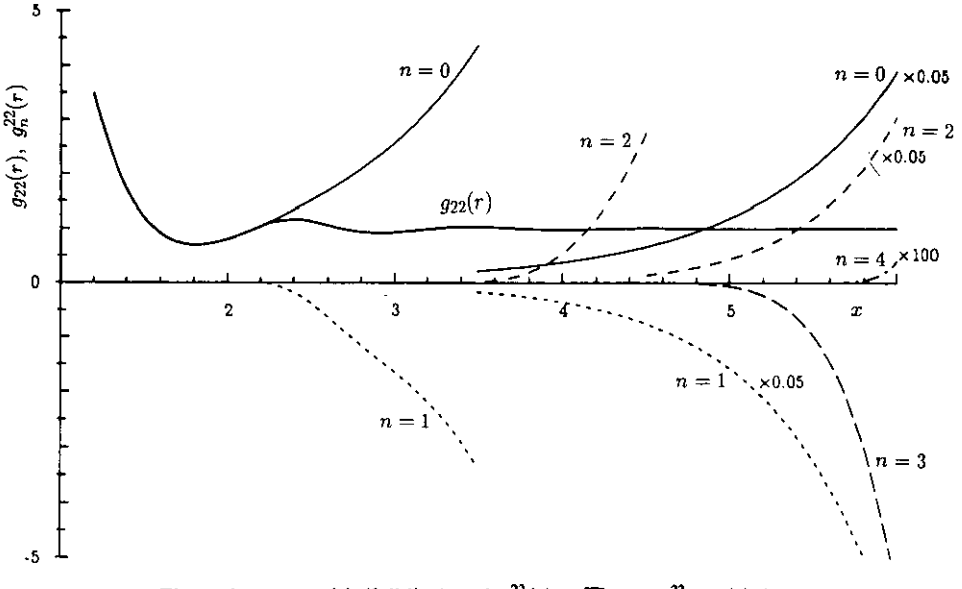

Figure 1. PDFs $g_{22}(r)$ (full line) and $g_n^{22}(r) = \sum_{\alpha_1,\alpha_2} g^{22}_{n,\alpha_1\alpha_2}(r)$ for $n = 0,\ldots,4$, for the binary HS system, defined via the parameters $R_1 = 1$, $R_2 = 1.2$, $c_1 = 0.9$ and $\eta = 0.6$. The different functions are labelled by the respective multiplier, unless it is unity.

We finally turn to the expressions for $g_{12}(r)$. We define, for reasons given below,

$$u(t) = tL_3(t) \tag{28}$$

and obtain for $g_{12}(r)$

$$rg_{12}(r) = \sum_{n=0}^{\infty} \frac{1}{2\pi i} \int \frac{1}{[S(t)]^{n+1}} \sum_{\alpha_1,\alpha_2} tu(t)\tilde{Q}_{n,\alpha_1\alpha_2}(t) \exp\{t[r - (\alpha_1 R_1 + \alpha_2 R_2)/2]\}\, dt$$
$$\alpha_1 = 1, \ldots, 2n+1 \ (2) \qquad \alpha_2 = 2n+2-\alpha_1, \ldots, 2n+1 \ (2) \tag{29}$$

where '(2)' in the range of the α_i means 'every second value'. Again the $\tilde{Q}_{n,\alpha_1\alpha_2}(t)$ are products of $L_0(t), L_1(t)$ and $L_2(t)$. With the same argumentation as above we perform the complex integrations by means of the residue theorem

$$\tilde{R}^i_{n,\alpha_1\alpha_2} = \frac{1}{n!} \lim_{t \to t_i} \left(\frac{d^n}{dt^n} \left\{ (t-t_i)^{n+1} \frac{tu(t)\tilde{Q}_{n,\alpha_1\alpha_2} \exp[t(r-X)]}{S^{n+1}(t)} \right\} \right) \tag{30}$$

arriving at an expression similar to those of (21) and (26)

$$g^{12}_{n,\alpha_1\alpha_2}(r) = \frac{1}{n!} \sum_{i=1}^{4} a^i_n \exp\{t_i[r - (\alpha_1 R_1 + \alpha_2 R_2)/2]\} \sum_{j=0}^{n} \tilde{b}^{j,i}_{n,\alpha_1\alpha_2} [r - (\alpha_1 R_1 + \alpha_2 R_2)/2]^j$$
$$\alpha_1 = 1, \ldots, 2n+1 \ (2) \qquad \alpha_2 = 2n+2-\alpha_1, \ldots, 2n+1 \ (2). \tag{31}$$

The coefficients $\tilde{b}^{j,i}_{n,\alpha_1\alpha_2}$ and the explicit form of the $\tilde{Q}_{n,\alpha_1\alpha_2}(t)$ are compiled in the appendix. The subshell structure is given by

$$\tilde{S}_{n,\alpha_1\alpha_2} := \{r \mid r \geqslant (\alpha_1 R_1 + \alpha_2 R_2)/2\}$$
$$1 \leqslant \alpha_1 \leqslant 2n+1 \ (2) \qquad 2n+2-\alpha_1 \leqslant \alpha_2 \leqslant 2n+1 \ (2). \tag{32}$$

The remarks made about the subshell structure for the 1–1 case holds, of course, also for the 2–2 and 1–2 subshells, despite of the different construction prescriptions.

Since the explicit determination of the coefficients a^i_n, $b^{j,i}_{n,\alpha_1\alpha_2}$, $\tilde{b}^{j,i}_{n,\alpha_1\alpha_2}$ and $\bar{b}^{j,i}_{n,\alpha_1\alpha_2}$ in (22), (26) and (31) is a rather technical problem, we have transferred it to the appendix.

The expressions for the $g^{ij}_{n,\alpha_1\alpha_2}(r)$ in (22), (26) and (31), as well as the prescriptions of how to calculate the coefficients a^i_n, $b^{j,i}_{n,\alpha_1\alpha_2}$, $\tilde{b}^{j,i}_{n,\alpha_1\alpha_2}$ and $\bar{b}^{j,i}_{n,\alpha_1\alpha_2}$ are sufficient to calculate the PDFs $g_{ij}(r)$ for any r; we have evaluated the expressions up to $n = 6$, a value which might be considered as a good compromise: on the one hand the expressions have become rather complex and might therefore be affected by some loss in numerical accuracy; on the other hand, up to this n-value the procedure is about as economical as the AE (cf section 2.2).

Concluding this chapter we want to point out the advantages of this method compared to the former approach by Leonard *et al* [25]: when working out the expressions presented in the appendix we have tried to find out as many parallels between the three cases (1–1, 2–2 and 1–2). This we have done firstly by separating—when calculating the residua (19)—into two parts: one containing $S(t)$, $u(t)$, t and its derivatives and the other containing the $L_i(t)$'s. The first part is identical for all three cases, which saves a lot of computing time since these expressions have to be evaluated only once. The second part has the same algebraic structure for all three cases and, in addition, many terms occurring in these expressions may be found more than once, making the algorithm even more economical. All the derivatives with respect to t, occurring in these expressions have been calculated to the highest possible order even though in most cases it would not be necessary due to the actual algebraic degrees of $L_i(t)$, $S(t)$ and $u(t)$ in t; this was done foreseeing an extension of this method to an HSY1 system, where these polynomials are throughout of two degrees higher than in the HS case. These results will be published elsewhere [26].

2.2. The asymptotic method

Let us start again with the Laplace-transforms $\hat{g}_{ij}(t)$ in equations (1)–(3). The direct representation of $rg_{ij}(r)$ by means of a contour integral (inverse Laplace transform formula) is:

$$rg_{ij}(r) = \frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} \frac{N_{ij}(t)}{D(t)} e^{tr} dt \tag{33}$$

where δ is an arbitrary positive number (the poles of $\hat{g}_{ij}(t)$ must be in the LHP).

For $r < R_{ij}$ we can evaluate the integral (33) by using a contour integration in the RHP and we obtain $g_{ij}(r) = 0$. For $r > R_{ij}$ we have to use a contour closing in the LHP. In general $D(t)$ will have an infinite number of zeros in the LHP. The contributions of the residues from all these poles of $\hat{g}_{ij}(t)$ will give a series representation of $rg_{ij}(r)$. It is easy to check that the $\hat{g}_{ij}(t)$ have a double pole for $t = 0$, contributing 1 to the $g_{ij}(r)$. The other poles have to be determined numerically as the zeros of the function $D(t)$. In the one-component case all the poles are simple [26]. In the two-component case an additional double pole ($\bar{t}$) (lying on the negative real axis) appears. The other poles are simple and occur in conjugate pairs (t_n, t_n^*).

Thus, we can write the PDFs as:

$$g_{ij}(r) = 1 + \sum_n h_{ij}^{(n)}(r) + H_{ij}(r) \tag{34}$$

where

$$h_{ij}^{(n)}(r) = \frac{1}{r}\lim_{t\to t_n}(t - t_n)\frac{N_{ij}(t)}{D(t)} e^{tr} + \frac{1}{r}\lim_{t\to t_n^*}(t - t_n^*)\frac{N_{ij}(t)}{D(t)} e^{tr} \tag{35}$$

and

$$H_{ij}(r) = \frac{1}{r}\lim_{t\to\bar{t}} e^{tr}\left\{\frac{d}{dt}\frac{(t-\bar{t})^2 N_{ij}(t)}{D(t)} + \frac{(t-\bar{t})^2 N_{ij}}{D(t)} r\right\} \tag{36}$$

are the contributions of the pair of simple poles and of the (possible) double pole on the negative real axis.

Since a simple (or a double) pole of $\hat{g}_{ij}(t)$ corresponds to a simple (or double) zero of $D(t)$, we obtain, by expanding the denominator in Taylor's series around t_n,

$$D(t) = D_1(t_n)(t - t_n) + \tfrac{1}{2}D_2(t_n)(t - t_n)^2 + O((t - t_n)^3) \tag{37}$$

where

$$\begin{aligned} D_1(t_n) = {} & L_0'(t_n) - [L_1'(t_n) + R_1 L_1(t_n)]\, e^{t_n R_1} - [L_2'(t_n) + R_2 L_2(t_n)]\, e^{t_n R_2} \\ & + [S'(t_n) + (R_1 + R_2)S(t_n)]\, e^{t_n(R_1+R_2)} \end{aligned} \tag{38}$$

$$\begin{aligned} D_2(t_n) = {} & L_0''(t_n) - [L_1''(t_n) + 2R_1 L_1'(t_n) + R_1^2 L_1(t_n)]\, e^{t_n R_1} \\ & - [L_2''(t_n) + 2R_2 L_2'(t_n) + R_2^2 L_2(t_n)]\, e^{t_n R_2} \\ & + [S''(t_n) + 2(R_1 + R_2)S'(t_n) + (R_1 + R_2)^2 S(t_n)]\, e^{t_n(R_1+R_2)} \end{aligned} \tag{39}$$

from which we obtain

$$h_{ij}^{(n)}(r) = 2\Re\left(\frac{N_{ij}(t_n)}{D_1(t_n)}\frac{e^{t_n r}}{r}\right) \tag{40}$$

and

$$H_{ij}(r) = 2\left(r\frac{N_{ij}(\tilde{t})}{D_2(\tilde{t})} + \frac{N'_{ij}(\tilde{t})D_2(\tilde{t}) - N_{ij}(\tilde{t})D'_2(\tilde{t})}{D_2^2(\tilde{t})}\right)\frac{e^{\tilde{t}r}}{r}. \tag{41}$$

The zeros of $D(t)$ have to be found numerically. However, the study of the dependence of the distribution of the zeros on the parameters of the system (i.e. R_1, R_2, η and c_1) helps to determine efficient starting points for the numerical solution of the non-linear equation $D(t) = 0$.

In figure 2 we show a typical distribution of the first few zeros of $D(t)$ around the origin for the same system as in figure 1. In general, in a two-component system we find two branches of zeros of $D(t)$. One, the closest to the imaginary axis, goes into the set of the zeros of the corresponding denominator for the one-component system in the appropriate limit. The other one, the leftmost, contains the non-trivial double zero and moves away from the imaginary axis in the same limit. In general, the contributions of the poles will decrease exponentially by increasing the distance from the imaginary axis.

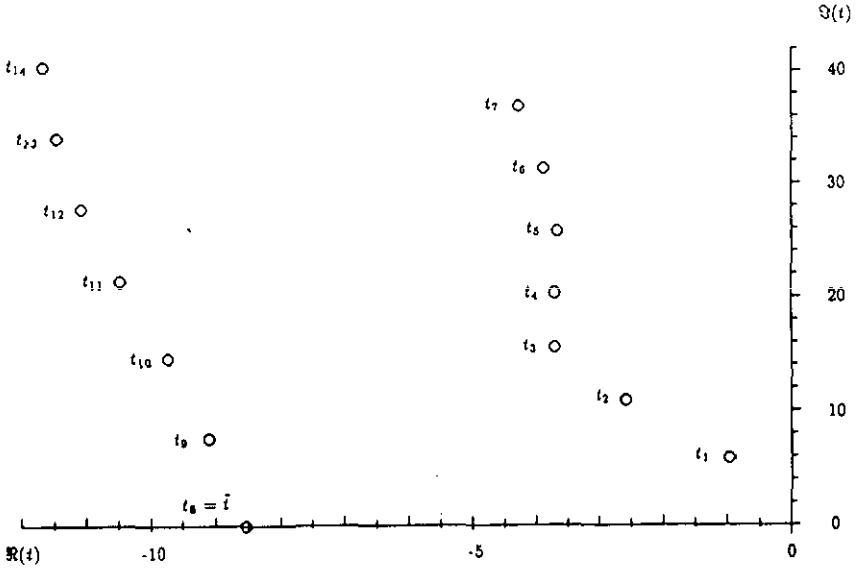

Figure 2. Distribution of the first fourteen poles t_i (i.e. zeros of $D(t)$ of (7)) for the same system as in figure 1.

Thus, it is enough to determine all the zeros of $D(t)$ in a rectangle to the left of the imaginary axis to evaluate the AE within a given precision. The property of $D(t)$ of being an entire function in every rectangle in the complex plane as well as the stable topology of the positions of its zeros greatly simplify the practical search for the zeros.

3. Comparison of the two methods

In this section we want to show how the formulae of the previous section can be used to evaluate the PDF over the whole r-range with very high precision. In addition, we briefly discuss the optimal choice of the best matching point as well as the relative efficiency of the two expressions.

In figure 3 we have depicted the differences between the PDFs $g_{ij}(r)$ calculated via the AE (taking into account an increasing number of poles) and the SE. We find in the example there shown as well as in other systems investigated that, up to the sixth shell included, the two methods are in excellent agreement. Proceeding to higher r-values the SE becomes less attractive: the expressions for the coefficients $a_n^i, b_{n,\alpha_1\alpha_2}^{j,i}, \tilde{b}_{n,\alpha_1\alpha_2}^{j,i}$ and $\bar{b}_{n,\alpha_1\alpha_2}^{j,i}$ become increasingly complicated, their evaluation becomes rather cumbersome and the corresponding implementation of these expressions rather difficult. The principal character of the SE was already demonstrated in figure 1: the subshell-PDFs $g_n^{ij}(r) = \sum_{\alpha_1,\alpha_2} g_{n,\alpha_1\alpha_2}^{ij}(r)$ are all either positive or negative and for larger r-values these functions may reach a considerable magnitude. Since the $g_{ij}(r)$ are built up from differences of a sequence of positive and negative functions (and the number of these function increases in a nonlinear way with distance) it is not surprising that beyond a certain r-value numerical accuracy can no more be guaranteed. For example, for $r = 7$, the PDF $g_{22}(r)$ (of our example system) has a value of 1.0287, a value which is obtained by summing over 42 subshell PDFs $g_{n,\alpha_1\alpha_2}^{22}$, the largest of which have values of: $g_{0,01}^{22}(7) = 262.10$, $g_{1,11}^{22}(7) = -347.42$, $g_{1,02}^{22}(7) = -196.59$ and $g_{2,21}^{22}(7) = 148.34$. A further disadvantage of the SE for larger r-values stems from the computing time: the number of subshells which have to be included for a given r-value depends on the values of R_1 and R_2. This number increases in any case with r and enhances drastically the computing time. Therefore we may conclude that, for the cases relevant to usual applications, the SE is no more attractive for r-values beyond the sixth shell.

With the AE we have the following advantages: the computing effort is constant or even decreasing with increasing distance (asymptotically, only the pole closest to the imaginary axis contributes to the value of $g_{ij}(r)$). The expressions needed are simple and straightforward to implement. However, the poles have to be found numerically and near the contact quite a large number of poles has to be taken into account. However, figure 3 demonstrates that in practical applications only a limited number of poles has to be included if the PDFs are required for distances larger than, e.g., three diameters. Including more than seven poles in our example does not change the result. This is not surprising, since it may be shown that the difference in magnitude of the contributions of two poles depends on the exponent of their real parts. Looking at figure 2 we see that there is a rather large gap between the first seven poles and the remaining poles, resulting in practically negligible contributions of the poles $\tilde{t} = t_8$ and the t_i, $i = 9, 10, \ldots$. Moreover, the other poles which belong to the same branch as t_i, $i = 1, \ldots, 7$, make also a negligible contribution to the total PDF.

In general, the number of poles that have to be taken into account to get a given precision inside a shell is a function of the physical parameters (i.e. the packing fraction, the concentration and the ratio of diameters). However, we have numerically checked that, within the physically interesting range ($0.1 \leqslant c_1 \leqslant 0.9$, $1.01 \leqslant R_2/R_1 \leqslant 1.6$ and $0.01 \leqslant \eta \leqslant 0.6$), the maximum relative difference between the $g_{ij}(r)$ obtained from the AE and the SE formulae remains less than 1% in the sixth shell if contributions from the first six poles have been summed. This means that for all the practical purposes one can safely use the SE up the sixth shell and the AE with

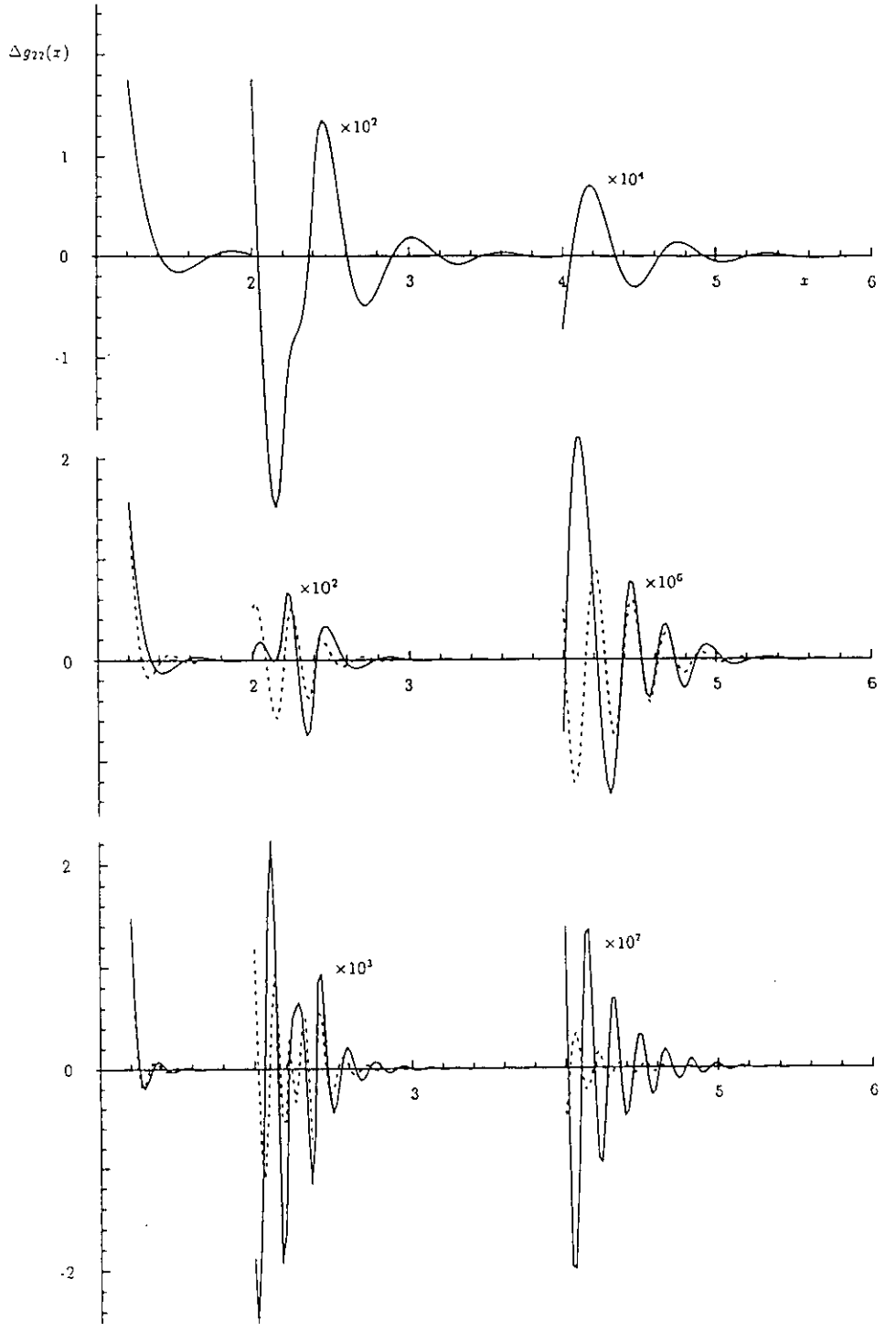

Figure 3. Difference of the PDFs $g_{22}^{\mathrm{SE}}(r)$ and $g_{22}^{\mathrm{AE},n}(r)$ (including n poles), for the HS system defined in figure 1. The line symbols are: $n = 1$ (upper panel), $n = 2$ (full line) and $n = 4$ (dotted line) (middle panel) and $n = 6$ (full line) and $n = 7$ (dotted line) (bottom panel). Again multipliers are indicated.

up to six poles from the seventh shell onward. With these parameters, a reasonable compromise is obtained between the opposite requirements of accuracy and velocity.

We intend to give a detailed discussion of the numerical implementations and a full evaluation of the computational efficiency elsewhere [28].

4. Conclusions

In this paper we have presented two complementary methods which furnish an accurate and efficient mean to determine the PDFs of an additive binary HS system over the whole r-range. These methods, which are based on the knowledge of the analytic expressions of the Laplace transforms of the PDFs perform the inversion in two different ways. Each of these methods is preferably used in a particular range of distances, being less reliable or not practical in the complementary range. In the intermediate range both methods may be applied successfully and can be matched to give perfect numerical agreement. These methods provide a powerful tool to evaluate the PDFs of binary hard-core mixtures in a very rapid and efficient way. They can be used in variational or perturbative calculations or other tasks in liquid-state physics. In this paper we have put particular effort in presenting expressions general enough to allow an easy extension to the binary HSYk system, where the analytic expressions have the same algebraic form.

Acknowledgments

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Appendix

The parameters a_n^i, $b_{n,\alpha_1\alpha_2}^{j,i}$, $\tilde{b}_{n,\alpha_1\alpha_2}^{j,i}$ and $\bar{b}_{n,\alpha_1\alpha_2}^{j,i}$ are determined by evaluating residues. We generalize (19) and (30) to a unified expression

$$R_{n,\alpha}^i = \frac{1}{n!}\lim_{t\to t_i}\left(\frac{\mathrm{d}^n}{\mathrm{d}t^n}\left\{(t-t_i)^{n+1}\frac{tu(t)Q_{n,\alpha_1\alpha_2}\exp[t(r-X)]}{S^{n+1}(t)}\right\}\right) \tag{A1}$$

where for the 1–1 and 2–2 case we simply put

$$u(t) = 1 \tag{A2}$$

and for the 1–2 case we use $u(t)$ of (28). (Even though $u(t)$ is for the binary HS case a polynomial of order two or less, we take into account in the following formalism derivatives of all orders, since these expressions may be required in applications to other systems, as e.g. in a HSYk-system). We perform the derivatives in (A1), leaving for the moment the polynomials $Q_{n,\alpha_1\alpha_2}(t)$ unspecified. The obtained expressions are grouped in powers of $[r-(\alpha_1R_1+\alpha_2R_2)]$ for the 1–1 and 2–2 cases and in powers of

$[r-(\alpha_1 R_1+\alpha_2 R_2)/2]$ for the 1–2 case, giving us the coefficients a_n^i and $b_{n,\alpha_1\alpha_2}^{j,i}, \bar{b}_{n,\alpha_1\alpha_2}^{j,i}$ and $\bar{b}_{n,\alpha_1\alpha_2}^{j,i}$. We separate the residues (A1) into two factors: one part containing $S(t)$, $u(t)$ and t and their respective derivatives and the other containing $Q_{n,\alpha_1\alpha_2}(t)$ and their derivatives. The first simplification is done by defining a common factor for all three cases and for every n:

$$a_n^i = \frac{1}{n!}\frac{1}{S^{n+1}(t)} \qquad n=0,1,\ldots. \tag{A3}$$

Note that an upper index i means here and in the following equations evaluation of the right-hand side for $t=t_i$.

Leaving the $Q_{n,\alpha_1\alpha_2}(t)$ for the moment unspecified, we obtain the formulae (A4) to (A10) as follows: for the like cases u has to be put to unity; for the 1–1 case the Q's are defined in (A14). The 2–2 expressions are obtained by simply putting a tilde ($\sim$) over the b's and Q's (from (A15)). The 1–2 case is discussed below. We obtain the following expressions for $n=0,\ldots,6$, omitting the argument in the polynomials:

$n=0$

$$b_{0,\alpha_1\alpha_2}^{0,i} = Q_{0,\alpha_1\alpha_2} ut \tag{A4}$$

$n=1$

$$b_{1,\alpha_1\alpha_2}^{1,i} = Q_{1,\alpha_1\alpha_2} ut \qquad b_{1,\alpha_1\alpha_2}^{0,i} = Q_{1,\alpha_1\alpha_2} c_1 + Q'_{1,\alpha_1\alpha_2} ut \tag{A5}$$

$n=2$

$$\begin{aligned} b_{2,\alpha_1\alpha_2}^{2,i} &= Q_{2,\alpha_1\alpha_2} ut \qquad & b_{2,\alpha_1\alpha_2}^{1,i} &= Q_{2,\alpha_1\alpha_2} c_2 + 2Q'_{2,\alpha_1\alpha_2} ut \\ b_{2,\alpha_1\alpha_2}^{0,i} &= -(Q_{2,\alpha_1\alpha_2} c_3 - Q'_{2,\alpha_1\alpha_2} c_2 - Q''_{2,\alpha_1\alpha_2} ut) \end{aligned} \tag{A6}$$

$n=3$

$$\begin{aligned} b_{3,\alpha_1\alpha_2}^{3,i} &= Q_{3,\alpha_1\alpha_2} ut \qquad & b_{3,\alpha_1\alpha_2}^{2,i} &= 3(Q_{3,\alpha_1\alpha_2} c_4 + Q'_{3,\alpha_1\alpha_2} ut) \\ b_{3,\alpha_1\alpha_2}^{1,i} &= -(Q_{3,\alpha_1\alpha_2} c_6 - 6Q'_{3,\alpha_1\alpha_2} c_4 - 3Q''_{3,\alpha_1\alpha_2} ut) \\ b_{3,\alpha_1\alpha_2}^{0,i} &= -(Q_{3,\alpha_1\alpha_2} c_8 + Q'_{3,\alpha_1\alpha_2} c_6 - 3Q''_{3,\alpha_1\alpha_2} c_4 - Q'''_{3,\alpha_1\alpha_2} ut) \end{aligned} \tag{A7}$$

$n=4$

$$\begin{aligned} b_{4,\alpha_1\alpha_2}^{4,i} &= Q_{4,\alpha_1\alpha_2} ut \qquad & b_{4,\alpha_1\alpha_2}^{3,i} &= 2(Q_{4,\alpha_1\alpha_2} c_7 + 2Q'_{4,\alpha_1\alpha_2} ut) \\ b_{4,\alpha_1\alpha_2}^{2,i} &= -(5Q_{4,\alpha_1\alpha_2} c_9 - 6Q'_{4,\alpha_1\alpha_2} c_7 - 6Q''_{4,\alpha_1\alpha_2} ut) \\ b_{4,\alpha_1\alpha_2}^{1,i} &= -(5Q_{4,\alpha_1\alpha_2} c_{12} + 10Q'_{4,\alpha_1\alpha_2} c_9 - 6Q''_{4,\alpha_1\alpha_2} c_7 - 4Q'''_{4,\alpha_1\alpha_2} ut) \\ b_{4,\alpha_1\alpha_2}^{0,i} &= -(Q_{4,\alpha_1\alpha_2} c_{15} + 5Q'_{4,\alpha_1\alpha_2} c_{12} + 5Q''_{4,\alpha_1\alpha_2} c_9 - 2Q'''_{4,\alpha_1\alpha_2} c_7 - Q^{IV}_{4,\alpha_1\alpha_2} ut) \end{aligned} \tag{A8}$$

$n=5$

$$\begin{aligned} b_{5,\alpha_1\alpha_2}^{5,i} &= Q_{5,\alpha_1\alpha_2} ut \qquad & b_{5,\alpha_1\alpha_2}^{4,i} &= 5(Q_{5,\alpha_1\alpha_2} c_{10} + Q'_{5,\alpha_1\alpha_2} ut) \\ b_{5,\alpha_1\alpha_2}^{3,i} &= -5(Q_{5,\alpha_1\alpha_2} c_{16} - 4Q'_{5,\alpha_1\alpha_2} c_{10} - 2Q''_{5,\alpha_1\alpha_2} ut) \\ b_{5,\alpha_1\alpha_2}^{2,i} &= -5(3Q_{5,\alpha_1\alpha_2} c_{19} + 3Q'_{5,\alpha_1\alpha_2} c_{16} - 6Q''_{5,\alpha_1\alpha_2} c_{10} - 2Q'''_{5,\alpha_1\alpha_2} ut) \\ b_{5,\alpha_1\alpha_2}^{1,i} &= -(Q_{5,\alpha_1\alpha_2} c_{22} + 30Q'_{5,\alpha_1\alpha_2} c_{19} + 15Q''_{5,\alpha_1\alpha_2} c_{16} - 20Q'''_{5,\alpha_1\alpha_2} c_{10} - 5Q^{IV}_{5,\alpha_1\alpha_2} ut) \\ b_{5,\alpha_1\alpha_2}^{0,i} &= -(Q_{5,\alpha_1\alpha_2} c_{25} + Q'_{5,\alpha_1\alpha_2} c_{22} + 15Q''_{5,\alpha_1\alpha_2} c_{19} + 5Q'''_{5,\alpha_1\alpha_2} c_{16} \\ &\quad - 5Q^{IV}_{5,\alpha_1\alpha_2} c_{10} - Q^{V}_{5,\alpha_1\alpha_2} ut) \end{aligned} \tag{A9}$$

$n = 6$

$$b^{6,i}_{6,\alpha_1\alpha_2} = Q_{6,\alpha_1\alpha_2}ut \qquad b^{5,i}_{6,\alpha_1\alpha_2} = 3(Q_{6,\alpha_1\alpha_2}c_{17} + 2Q'_{6,\alpha_1\alpha_2}ut)$$

$$b^{4,i}_{6,\alpha_1\alpha_2} = -5(7Q_{6,\alpha_1\alpha_2}c_{24} - 3Q'_{6,\alpha_1\alpha_2}c_{17} - 3Q''_{6,\alpha_1\alpha_2}ut)$$

$$b^{3,i}_{6,\alpha_1\alpha_2} = -5(7Q_{6,\alpha_1\alpha_2}c_{26} + 28Q'_{6,\alpha_1\alpha_2}c_{24} - 6Q''_{6,\alpha_1\alpha_2}c_{17} - 4Q'''_{6,\alpha_1\alpha_2}ut)$$

$$b^{2,i}_{6,\alpha_1\alpha_2} = -(7Q_{6,\alpha_1\alpha_2}c_{29} + 105Q'_{6,\alpha_1\alpha_2}c_{26} + 210Q''_{6,\alpha_1\alpha_2}c_{24} - 30Q'''_{6,\alpha_1\alpha_2}c_{17} - 15Q^{IV}_{6,\alpha_1\alpha_2}ut)$$

$$b^{1,i}_{6,\alpha_1\alpha_2} = -(7Q_{6,\alpha_1\alpha_2}c_{34} + 14Q'_{6,\alpha_1\alpha_2}c_{29} + 105Q''_{6,\alpha_1\alpha_2}c_{26} + 140Q'''_{6,\alpha_1\alpha_2}c_{24} - 15Q^{IV}_{6,\alpha_1\alpha_2}c_{17} - 6Q^{V}_{6,\alpha_1\alpha_2}ut)$$

$$b^{0,i}_{6,\alpha_1\alpha_2} = -(Q_{6,\alpha_1\alpha_2}c_{38} + 7Q'_{6,\alpha_1\alpha_2}c_{34} + 7Q''_{6,\alpha_1\alpha_2}c_{29} + 35Q'''_{6,\alpha_1\alpha_2}c_{26} + 35Q^{IV}_{6,\alpha_1\alpha_2}c_{24} - 3Q^{V}_{6,\alpha_1\alpha_2}c_{17} - Q^{VI}_{6,\alpha_1\alpha_2}ut) \tag{A10}$$

where the c_i are defined for both cases:

$$c_1 = 1 - tS_2/S_1$$
$$c_2 = 2 - 3tS_2/S_1$$
$$c_3 = (tS_3 + 3S_2c_1)/S_1$$
$$c_4 = 1 - 2tS_2/S_1$$
$$c_5 = 4 - 5tS_2/S_1$$
$$c_6 = (4tS_3 + 3S_2c_5)/S_1$$
$$c_7 = 2 - 5tS_2/S_1$$
$$c_8 = (tS_4 + 2S_3c_7 - 15S_2^2/S_1c_1)/S_1$$
$$c_9 = (2tS_3 + 3S_2c_2)/S_1$$
$$c_{10} = 1 - 3tS_2/S_1$$
$$c_{11} = 6 - 7tS_2/S_1$$
$$c_{12} = (tS_4 + 4S_3c_{10} - 3S_2^2/S_1c_{11})/S_1$$
$$c_{13} = 4 - 7tS_2/S_1$$
$$c_{14} = (2tS_3 + 3S_2c_{13})/S_1$$
$$c_{15} = (tS_5 + 5S_4c_{10} - 5S_3c_{14} + 105S_2^3/S_1^2c_1)/S_1$$
$$c_{16} = (4tS_3 + 3S_2c_{13})/S_1$$
$$c_{17} = 2 - 7tS_2/S_1$$
$$c_{18} = 3 - 4tS_2/S_1$$
$$c_{19} = (tS_4 + 2S_3c_{17} - 7S_2^2/S_1c_{18})/S_1$$
$$c_{20} = 8 - 9tS_2/S_1$$
$$c_{21} = (tS_3 + 6S_2c_4)/S_1$$
$$c_{22} = (6tS_5 + 15S_4c_{17} - 70S_3c_{21} + 105S_2^3/S_1^2c_{20})/S_1$$
$$c_{23} = 1 - 4tS_2/S_1$$
$$c_{24} = (tS_3 + 3S_2c_4)/S_1$$
$$c_{25} = (tS_6 + 3S_5c_{17} - 35S_4c_{24} + 70S_3/S_1(-S_3c_{23} + 6S_2^2/S_1c_2) - 945S_2^4/S_1^3c_1)/S_1$$
$$c_{26} = (tS_4 + 4S_3c_{23} - 12S_2^2/S_1c_2)/S_1$$
$$c_{27} = 4 - 9tS_2/S_1$$

$$
\begin{aligned}
c_{28} &= (2tS_3 + 3S_2c_{27})/S_1 \\
c_{29} &= (3tS_5 + 15S_4c_{23} - 20S_3c_{28} + 135S_2^3/S_1^2c_5)/S_1 \\
c_{30} &= (4tS_3 + 3S_2c_{27})/S_1 \\
c_{31} &= 2 - 9tS_2/S_1 \\
c_{32} &= 3 - 5tS_2/S_1 \\
c_{33} &= 10 - 11tS_2/S_1 \\
c_{34} &= (tS_6 + 6S_5c_{23} - 10S_4c_{30} + 40S_3/S_1(-S_3c_{31} + 9S_2^2/S_1c_{32}) - 135S_2^4/S_1^3c_{33})/S_1 \\
c_{35} &= (tS_4 + 4S_3c_{31} - 18S_2^2/S_1c_{32})/S_1 \\
c_{36} &= (2tS_3 + 9S_2c_7)/S_1 \\
c_{37} &= 8 - 11tS_2/S_1 \\
c_{38} &= (tS_7 + 7S_6c_{23} - 14S_5c_{30} - 35S_4c_{35} + 35S_3/S_1(4S_3c_{36} - 45S_2^3/S_1^2c_{37}) \\
&\quad + 10395S_2^5/S_1^4c_1)/S_1
\end{aligned}
\tag{A11}
$$

and S_i stands for the ith derivative of $S(t)$.

For the determination of the $\bar{b}^{j,i}_{n,\alpha_1\alpha_2}$ we can use the same equations (A4)–(A10), simply replacing the c_i's by the d_i's (defined below) and the Q's by $\tilde{Q}$'s (cf (A15)):

$$
\begin{aligned}
&d_1 = uc_1 + u't \qquad d_2 = uc_2 + 2u't \qquad d_3 = uc_3 - u'c_2 - u''t \\
&d_4 = uc_4 + u't \qquad d_6 = uc_6 - 6u'c_4 - 3u''t \qquad d_7 = uc_7 + 2u't \\
&d_8 = uc_8 + u'c_6 - 3u''c_4 - u'''t \qquad d_9 = uc_9 - \tfrac{6}{5}u'c_7 - \tfrac{6}{5}u''t \\
&d_{10} = uc_{10} + u't \qquad d_{12} = uc_{12} + 2u'c_9 - \tfrac{6}{5}u''c_7 - \tfrac{4}{5}u'''t \\
&d_{15} = uc_{15} + 5u'c_{12} + 5u''c_9 - 2u'''c_7 - u^{IV}t \qquad d_{16} = uc_{16} - 4u'c_{10} - 2u''t \\
&d_{17} = uc_{17} + 2u't \qquad d_{19} = uc_{19} + u'c_{16} - 2u''c_{10} - \tfrac{2}{3}u'''t \\
&d_{22} = uc_{22} + 30u'c_{19} + 15u''c_{16} - 20u'''c_{10} - 5u^{IV}t \\
&d_{24} = uc_{24} - \tfrac{3}{7}u'c_{17} - \tfrac{3}{7}u''t \\
&d_{25} = uc_{25} + u'c_{22} + 15u''c_{19} + 5u'''c_{16} - 5u^{IV}c_{10} - u^{V}t \\
&d_{26} = uc_{26} + 4u'c_{24} - \tfrac{6}{7}u''c_{17} - \tfrac{4}{7}u'''t \\
&d_{29} = uc_{29} + 15u'c_{26} + 30u''c_{24} - \tfrac{30}{7}u'''c_{17} - \tfrac{15}{7}u^{IV}t \\
&d_{34} = uc_{34} + 2u'c_{29} + 15u''c_{26} + 20u'''c_{24} - \tfrac{15}{7}u^{IV}c_{17} - \tfrac{6}{7}u^{V}t \\
&d_{38} = uc_{38} + 7u'c_{34} + 7u''c_{29} + 35u'''c_{26} + 35u^{IV}c_{24} - 3u^{V}c_{17} - u^{VI}t
\end{aligned}
\tag{A12}
$$

(the c_i are those from equations (A11); the d_i not mentioned in (A12) are not required).

For the 1–1 case the $Q_{n,\alpha_1\alpha_2}(t)$ are given by

$$
\begin{aligned}
Q_{n,\alpha_1\alpha_2}(t) &= (-1)^{(\alpha_1+\alpha_2+n)}\binom{n}{\alpha_1 - 1}\binom{\alpha_1}{\alpha_1 + \alpha_2 - (n+1)} \\
&\quad \times L_0^{\alpha_1+\alpha_2-(n+1)}(t)L_1^{n+1-\alpha_1}(t)L_2^{n+1-\alpha_2}(t)
\end{aligned}
\tag{A13}
$$

in the 2–2 case we find

$$
\begin{aligned}
\tilde{Q}_{n,\alpha_1\alpha_2}(t) &= (-1)^{(\alpha_1+\alpha_2+n)}\binom{n}{\alpha_2 - 1}\binom{\alpha_2}{\alpha_1 + \alpha_2 - (n+1)} \\
&\quad \times L_0^{\alpha_1+\alpha_2-(n+1)}(t)L_1^{n+1-\alpha_1}(t)L_2^{n+1-\alpha_2}(t)
\end{aligned}
\tag{A14}
$$

and finally for the 1–2 case we have the following expression

$$\tilde{Q}_{n,\alpha_1\alpha_2}(t) = (-1)^{[(\alpha_1+\alpha_2)/2+n+1]} \times \binom{n}{(2n+1)-(\alpha_1+\alpha_2)/2} \binom{(2n+1)-(\alpha_1+\alpha_2)/2}{(2n+1-\alpha_1)/2} \times L_0^{(\alpha_1+\alpha_2)/2-(n+1)}(t) L_1^{(2n+1-\alpha_1)/2}(t) L_2^{(2n+1-\alpha_2)/2}(t). \tag{A15}$$

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